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Quantitative thermal characterization of carbon-epoxy composites using differential scanning calorimetry and thermogravimetric analysis

D. Noël, J.-J. Hechler, K.C. Cole

Industrial Materials Research Institute
National Research Council Canada
75, boul. de Mortagne
Boucherville, Québec
Canada, J4B 6Y4

A. Chouliotis, K.C. Overbury

Canadair Ltd.
P.O. Box 6087
Montréal, Québec
Canada, H3C 3G9

ABSTRACT

A differential scanning calorimetry (DSC) method has been developed to characterize carbon-epoxy prepregs. DSC was done with nitrogen as the atmosphere in order to avoid the oxidation reactions which degrade the epoxy resin during heating. Since the resin distribution in a given batch of prepreg is not entirely uniform, and since the sample used for DSC is relatively small, the percentage of resin may vary significantly from sample to sample, even though they are taken from the same sheet of prepreg. Hence, the exact resin content must be determined for each sample in order to obtain reproducible values for the curing enthalpy. A thermogravimetric (TG) method using an oxidizing atmosphere has been developed for this purpose. After the DSC experiment, a TG analysis is done on the same sample. The exact mass of resin is found on the TG curve at the inflexion point corresponding to the end of oxidation of the epoxy resin and to the beginning of oxidation of the carbon fibres. For Narmco 5208/WC3000 prepreg, this inflexion point occurs at about 580°C. This procedure gives enthalpy values with a relative standard deviation smaller than 1%. The aging of the prepreg when exposed for 66 days at room temperature and 50% relative humidity was also studied using these thermal methods.

INTRODUCTION

Various analytical techniques have been used to characterize fibre-reinforced organic-matrix composites. The development of methods using high-performance liquid chromatography or Fourier transform infrared spectroscopy has been reported previously [1-2]. These techniques allow the monitoring of small variations in the chemical composition of an epoxy resin formulation. A pyrolysis - gas chromatographic (Py-GC) method has also been developed and applied to a carbon-epoxy prepreg [3]. This method involves a rapid heat transfer (~ 1000°C/s) to the sample in order to decompose the epoxy resin. Decomposition products are immediately injected and separated on a capillary gas chromatographic column. The chromatogram gives a unique chemical pattern of the epoxy resin which can be used to characterize the systems studied. Unfortunately, in Py-GC, the aging of a carbon-epoxy prepreg can be evaluated only if variations in the chemical composition of the resin are relatively large.

The usual methods of thermal analysis involving a slow transfer of heat to the sample (5 - 10 °C/min) also give useful information on the composition, structure and physicochemical behavior of epoxy-based prepreg. Among the different methods available, the most popular are differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA) [4,5]. In this work, only DSC and TGA will be considered.

These methods will be applied to the Narmco Rigidite 5208/WC3000 system, which has been described in detail elsewhere [6]. Briefly, the resin consists of three main components. The major epoxy (about 67% by weight) is a complex mixture of about 60% tetraglycidyl-4,4'-diaminodiphenylmethane

(TGDDM) and 40% oligomers and by-products. The second component (about 10% by weight) is the minor epoxy, a bisphenol A Novolac epoxy. Finally, the third component is 4,4'-diaminodiphenylsulphone (DDS) acting as a hardener (about 23% by weight).

There are some reports in the literature on the analysis of Narmco 5208 neat resin by DSC [7-9]. However, most of the work has been related to the determination of kinetic parameters of cure reactions involving the main epoxy (TGDDM) and the amine hardener (DDS). The main purpose of this work is to develop an accurate DSC method to characterize the Narmco 5208 prepreg and to compare this method to other analytical techniques in order to examine its advantages and disadvantages as a quality control method.

The application of heat to an epoxy resin system causes reactions between epoxy and hardener. The main goal of a DSC experiment is to evaluate the enthalpy corresponding to the curing reaction. However, with a carbon-epoxy prepreg, reproducibility in the determination of enthalpy is a major problem because the percentage of organic resin can vary significantly from sample to sample, even when they come from the same sheet of prepreg, due to nonuniform distribution of resin [9]. Organic solvent extractions of different samples taken from the same batch of prepreg likewise show a significant variation in the quantity of resin extracted [10]. In the case of Narmco 5208 prepreg, it varies from 40% to 46%. As the enthalpy is related to the epoxy resin only, it is important to find a method to accurately measure the content of resin in a sample after a DSC experiment. The mass of a typical sample varies from 30 to 40 mg. Assuming a carbon fibre content of about 60% by weight, the quantity of epoxy resin varies from 12 to 16 mg. Thus, the method used to evaluate the mass of resin must be precise in order to obtain accurate and reproducible enthalpy values.

The decomposition of the resin without oxidation of the fibre reinforcement can sometimes be achieved in an inert atmosphere and the quantity of resin can be found using a simple thermogravimetric analysis [4,5,11,12]. However, in practical terms, thermal decomposition with an inert gas such as nitrogen can create some problems. With some epoxy resin systems, the decomposition can be incomplete, leading to false results. Also, the decomposition of the resin in the absence of oxygen does not generate small molecules such as CO_2, CO or H_2O. Volatiles formed during the decomposition condense on the different parts of the instrument and contaminate the system. Thus, the possibility of using a TGA method with either oxygen or nitrogen as atmosphere has been examined. This method in conjunction with a DSC experiment performed under appropriate experimental conditions will give accurate values of enthalpy for the curing reaction.

EXPERIMENTAL SECTION

Materials

The composite system studied was the Rigidite 5208/WC3000 system sold by Narmco Materials, Inc. (Anaheim, CA, USA). The reinforcement consists of Celion carbon fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern. The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight. In addition to the prepreg, some neat samples were also used. The recommended cure schedule consists of a one-hour dwell at 135°C followed by a two-hour cure at 177°C.

All samples were stored in a freezer at all times except for sampling and performance of experiments.

Thermogravimetric Analysis

The thermobalance used was a Model B70 from SETARAM (Caluire, France), and is equipped with a carbon resistance furnace. Data are collected via a Hewlett-Packard system. The balance is precise to ±30 µg over a long period of time. The output signal of the balance in mV is transformed into mg using a sensitivity factor which is known to 0.3%. The loss of weight is thus measured within 0.3%.

Samples were analysed in either alumina or platinum crucibles. The heating rate was maintained constant at 10°C/min. For isothermal experiments, the temperature of the furnace was increased rapidly (25°C/min) to the selected temperature and maintained at this level.

Differential Scanning Calorimetry

The differential calorimeter was a SETARAM Model CDP111. It consists of an oven, an electronic temperature programmer, and a signal amplifier, and is interfaced with a Hewlett-Packard HP-85 microcomputer to store the raw data and to perform different mathematical treatments. The calorimeter is equipped with two heat flow sensors (Calvet type), one for the sample, the other for the reference, which are located in the centre of a thermostatted block. Each sensor consists of about 150 thermocouples almost completely surrounding a cylindrical sensitive zone (20 mm long, 7 mm in diameter). The calorimetric signal is the difference between the signals from the sample and the reference sensors.

Samples of prepreg (30-40 mg) were weighed in open platinum crucibles and suspended vertically in the calorimeter. An empty platinum

crucible was used as reference. The electrical signal in μV was transformed into mW (heat flow) by a fourth degree equation obtained from prior calibration of the instrument. In scanning mode, the signal in mW was recorded as a function of the real temperature of the sample. All scans were done at 5°C/min. The calculation of enthalpy was done by measuring the surface area under the DSC curve.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Nitrogen atmosphere

The easiest method to obtain the mass of resin in a carbon-epoxy prepreg is to pyrolyze the resin in an oven at constant temperature and to weigh the carbon fibres. Some epoxy systems undergo complete decomposition under nitrogen at appropriate temperatures [11,13]. Figure 1 shows the TG curve obtained with nitrogen for Narmco 5208 neat epoxy resin (batch 1023). The weight loss is fairly constant at 66.1% between 750°C and 900°C, and the curve shows that it is impossible to completely decompose this epoxy system in a nitrogen atmosphere below 1200°C.

A second sample of Narmco 5208 neat resin (from batch 1047) gave a weight loss of 66.9% under the same conditions. Since the percentage of decomposition at 900°C appears to be relatively constant, some attempts were made to determine the percentage of resin in the prepreg by isothermal decomposition. Samples of neat resin were put in an oven maintained at 900°C with nitrogen as atmosphere. Unfortunately, when the samples are put in the oven, the decomposition is so rapid that the resin overflows the

crucible and the loss of resin is significant. It is necessary to control the rise of temperature and thus, a thermobalance is simpler to use.

A TG curve of the carbon-epoxy prepreg with nitrogen will give the mass of the decomposed epoxy resin. This mass is known to 0.5%. A correction using the value found for the decomposition of the neat resin (~ 66%) will lead to the total mass of resin in the prepreg. The relative error of this correction is 1.5%. Thus, the total mass of resin will have a relative error of 2%. Typically, if the quantity of resin in the prepreg is about 20 mg, the absolute error on the mass is about 0.4 mg. This error is not negligible for the determination of accurate enthalpy values, and this method also requires that the composition of the epoxy resin be relatively constant in order to minimize the error involved in the correction.

Thus, in spite of the tendency of carbon to decompose in an oxidizing atmosphere, some TG curves were obtained for Narmco 5208 prepreg in an oxidizing environment in order to find a method which has a smaller relative error and is less sensitive to the chemical composition of the epoxy resin.

Oxygen atmosphere

The purpose of the following experiments was to find the optimum temperature for achieving the isothermal decomposition of epoxy resin without oxidation of carbon fibres. Initial thermograms were obtained in dynamic mode at a heating rate of 10°C/min with oxygen as atmosphere in order to localize the different decomposition steps. Thermograms for neat epoxy resin Narmco 5208 (batch 1023), for carbon fibres alone, and for carbon-epoxy prepreg (batch 1103) are shown in Figures 2, 3 and 4 respectively.

The derivative TG curve for the neat 5208 resin (Figure 2a) shows two distinct peaks indicating a two-step decomposition. Similar results have been reported in the literature for different epoxy systems [11,14]. The first decomposition begins at about 260°C and corresponds mainly to the release of volatile products. This step is characterized by the presence of a strong odour. The second decomposition is odourless an begins at about 450°C. It is associated with the oxidation of the carbonized residue. At 610°C, the resin is completely oxidized in an oxygen atmosphere.

The change of slope in the TG curve at about 460°C has been used to calculate the percentage of resin. Two points were selected as shown in Figure 2b. Point 1 corresponds to the inflexion point at 460°C and point 2 is the extrapolation of two sections of the curve as shown in the figure. These correspond respectively to 51.8% and 47.6%. Assuming that these points of decomposition are invariant, they can possibly be used to determine the percentage of resin.

Figure 3 shows that the decomposition of carbon fibres in oxygen is a one-step process. There is a slow oxidation up to 550°C followed by a much faster oxidation. By 670°C, they are completely oxidized.

The TG curve of the Narmco 5208 prepreg is given in Figure 4. The three decomposition steps observed in the previous figures are distinguishable. The first takes place below 450°C, and the second, which corresponds to the oxidation of carbonized epoxy resin, is observed between 450 and 600°C. Finally, the decomposition of carbon fibres is recorded between 600 and 780°C. The oxidation of the carbon fibres is displaced toward higher temperature when the fibres are embedded in the epoxy resin, as compared to the result obtained with fibres alone. In a prepreg, the reinforcing fabric is completely covered with epoxy resin and it is reasonable to assume that

the carbon fibres are not oxidized significantly until the resin coating has decomposed.

The epoxy resin without reinforcement is almost totally oxidized at about 600°C, the same temperature at which the carbon fibres begin to be oxidized. Thus, experiments were done to investigate the possibility of finding a temperature around 400 - 500°C which would allow isothermal decomposition of the epoxy resin without excessive oxidation of the carbon fibres.

The first experiment in isothermal mode was carried out at 500°C with Narmco 5208 prepreg, and Figure 5a shows the variation of the sample weight and of the furnace temperature as a function of time. An inflexion point is observable at 80 minutes and corresponds to a loss of weight of about 40%. It is known that this composite has about this percentage of epoxy resin. However, there is no stabilization of the weight of the sample as the time increases and this indicates a continuous oxidation of the carbon fibres. Thus, this temperature is too high to perform a well-defined isothermal decomposition of the prepreg.

The next experiment was done with the same prepreg at 460°C, and as in the previous case, the weight loss had not stabilized after three hours. The decomposition rate slows down when the weight loss is around 40%, but this temperature cannot give an accurate determination of the mass of the resin in the prepreg.

A third experiment was done at 420°C with a "synthetic" carbon-epoxy prepreg. This was prepared by mixing short carbon fibres and neat Narmco 5208 epoxy resin (batch 1023). The mixture contained 22.7 mg of carbon (34.8%) and 42.6 mg of resin (65.2%). The sample was maintained at 420°C for 7 hours and the curves are shown in Figure 5b. As previously, the weight

loss does not stabilize with time and this indicates oxidation of the carbon fibres. However, an enlargement of the last part of the curve shows a small inflexion point at 280 minutes. This point corresponds to a weight loss of 66.5% and is probably caused by the disappearance of the epoxy resin followed by a faster oxidation of the fibres. This percentage (66.5%) corresponds relatively well with the known percentage of resin (65.2%) but the difference is still larger than would be desirable for calculating accurate values of enthalpy. It is probable that due to the duration of the experiment, a significant percentage of carbon is oxidized, which increases the apparent percentage of resin found with the TG curve. Also, the inflexion point is extremely difficult to detect and the analysis time is too long to be practical.

It was observed in Figure 4 that there is an inflexion point at about 580°C which seems to correspond to the end of oxidation of the epoxy resin and to the beginning of oxidation of the carbon fibres. This point is near 40% weight loss, which is close to the expected resin content. Thus, some experiments were done with programmed temperature and well characterized samples in order to emphasize this inflexion point and to verify its relationship to the percentage of epoxy resin in the prepreg.

Four mixtures with known percentages of epoxy resin and carbon fibres were prepared and the TG curves were recorded up to 800°C in oxygen at a heating rate of 10°C/min. An example of a typical thermogram is given in Figure 6a. The curve is similar to that of Figure 4. The inflexion point just described is observable at about 565°C (point 3). This section of the TG curve is enlarged in Figure 6b. In addition to this point, the inflexion points labelled point 1 and point 2 in Figure 2 were also used to evaluate the percentage of resin. For these, the values found on the TG curve are divided by the values found with the neat epoxy resin (51.8% and 47.6%). Table 1

summarizes the results obtained with the prepared mixtures. Clearly, only the inflexion point 3 allows an accurate direct determination of the mass of resin in the sample. Thus, this point will be used for subsequent analyses.

The relative error of the mass determined using point 3 is evaluated as about 0.5%. For a typical value of 20 mg, the error is 0.1 mg. Thus, the mass determined with oxygen is more precise than the mass calculated from the isothermal experiment with nitrogen. The results in Table 1 demonstrate that this thermogravimetric determination of the mass of the resin in a prepreg is excellent and can be used to evaluate accurately the curing enthalpy of the epoxy resin.

Comparison of the TG curves of prepreg (batch 1103) and of a synthetic mixture (40.3% resin) shows that the inflexion point is displaced by about 25°C towards higher temperature for the prepreg. This variation is explained by a better coverage of carbon fibres in the prepreg than in the prepared mixture and also by the different form of the sample. It is well known that a sample with a low ratio of surface area to mass will often decompose more slowly than a sample of equal mass but consisting of very small particles [15]. As the prepreg is more dense and compact than the prepared mixture, it is reasonable to assume that the decomposition will be slower with the prepreg.

A comparison of the TG curve of carbon fibres (Figure 3) with Figures 4 and 6 indicates that at the inflexion point there is a possibility of oxidation of the carbon amounting to about 4% (at 565°C) for the synthetic mixture and about 15% (at 590°C) for the carbon-epoxy prepreg. For the prepared mixtures, it has been shown that the determination of the percentage of resin is not affected by the oxidation of the carbon fibres. However, for the prepreg, the extent of this oxidation might reach 15%, and is perhaps not

negligible, especially in areas where the resin is thinner. The percentage of resin in the composite as measured by TGA for different samples from various batches ranges from 40 to 47% as shown in Table 2. These values are similar to those found using an organic liquid extraction [10]. A significant oxidation of the carbon fibres would increase the apparent percentage of resin found in the prepreg by TGA, as compared to that found by solvent extraction, which does not seem to be the case here. Thus, it is believed that the determination of the mass of resin in the prepreg is not significantly affected by the oxidation of carbon, and the inflexion point (point 3) corresponds to the end of decomposition of the epoxy resin and to the beginning of oxidation of the carbon fibres.

Air atmosphere

An experiment was done with air as atmosphere in order to check whether this environment is sufficiently oxidizing to decompose the carbon-epoxy prepreg in three well-defined steps. The resulting TG curve and its derivative are shown in Figure 7. A comparison with Figure 4 clearly shows that the inflexion point detected at 590°C in oxygen is not observed on the TG curve obtained in air. It is probable that with air as atmosphere the supply of oxygen is not sufficient to rapidly decompose the resin. Since this results in different kinetics of decomposition compared to a pure oxygen atmosphere, the use of air instead of oxygen as atmosphere is not suitable for accurate determination of the mass of resin in the prepreg.

Differential Scanning Calorimetry

Optimization

Various experimental factors such as atmosphere, heating rate, weight error and area error can affect the reproducibility in DSC. Chen and Hunter [9] have shown that the variation in the determination of the enthalpy of polymerization for the neat epoxy resin Narmco 5208 is substantial without an optimized experimental procedure. The sampling of a piece of prepreg causes a large error in the evaluation of ΔH [16]. Morgan et al. found that the reproducibility for ΔH is better than 5% for samples taken in close proximity (<10 cm apart) in a prepreg lot. However, the relative standard deviation increases to 30% for samples taken from the same lot but separated by a distance greater than 20 cm, or for samples taken from different lots.

In addition, Narmco 5208 epoxy resin starts to decompose at a fairly low temperature and low-molecular-weight compounds are released during heating [17]. Propenal has been positively identified as a thermal decomposition product. Many other aldehydes are also formed during the curing or during the heating of the cured resin. This fact has been confirmed by TGA and DSC. At 320°C, which represents the upper limit for a DSC experiment, the TG curve shows that there is significant decomposition of the resin. Figure 8 shows the DSC curve of the same prepreg obtained in static air. After the curing peak, decomposition of the resin prevents the signal from returning to its level before curing. Thus, the determination of the enthalpy of the curing reaction is affected to some extent by decomposition reactions. It is important to minimize these reactions in order to obtain accurate DSC results.

Assuming that oxidation of the resin is an important part of the degradation reactions, the use of nitrogen as atmospheric gas during the DSC experiments can significantly reduce these reactions. Figure 9 compares TG curves up to 320°C obtained for the prepreg with nitrogen and oxygen as atmosphere. Under oxygen, the loss of weight is greater than 2% before curing occurs at 240°C. With nitrogen the weight loss is less than 1% at the same point. This loss is attributed mainly to the release of additives or impurities such as acetone [10] or methyl ethyl ketone [17]. Thermal degradation of the epoxy resin begins at 280°C. As the calculation of enthalpy from the DSC curve is usually done between 130°C and 273°C, it is assumed that the ΔH determined with nitrogen is almost totally related to the curing reaction between epoxy and hardener. Figure 10 illustrates the DSC curve of the prepreg obtained under nitrogen, together with the baseline obtained using empty crucibles. The signal from the calorimeter returns to its initial level after the curing of the resin.

In addition to the nitrogen atmosphere, it is important to use two paired crucibles in the calorimeter in order to obtain a stable baseline without curvature. These prerequisites are necessary to obtain reproducible enthalpy values.

Comparison of different batches of Narmco 5208

Several batches of Narmco 5208/WC3000 prepreg and neat resin were studied by DSC at a heating rate of 5°C/min with nitrogen as atmosphere. Samples were analyzed vertically in platinum cups. Thermograms for all the prepregs are similar to the curve given in Figure 10. After the DSC experiment, each sample was analysed by thermogravimetry at a heating

rate of 10°C/min with oxygen as atmosphere. Table 2 summarizes the results.

During DSC, some volatile products are released, and the percentage of weight lost during the experiment is given in the third column. This quantity is added to the amount of resin found by TGA to give the total resin content of the sample in question (column 4). The heat of reaction measured by DSC is then divided by the true resin weight to give the "corrected" enthalpy ΔH in joules per gram of resin (column 6). The "uncorrected" enthalpy values (column 5) were calculated using the nominal resin content of 42% for all samples.

The temperature at which the maximum of the DSC peak occurs varies only very slightly between 248°C and 250°C. The enthalpy values were calculated by integrating the DSC peak between 130°C and 273°C.

For three specimens from batch 1014, the mean uncorrected enthalpy is 554 J/g, with a standard deviation of 28 (5.0%), whereas the mean for the corrected enthalpy is 548 J/g with a standard deviation of 4 (0.6%). These results are in concordance with those reported by Morgan [16] who noted that an enthalpy variation of 5% is observed in the analysis of prepregs if samples are taken in close proximity on a lot. This was the case in our experiments. However, the correction using the exact mass of resin gives a relative standard deviation smaller than 1%.

If the percentage of resin in the prepreg is similar for two samples, the values of enthalpy are relatively reproducible even without correction. For example, this is observed for batches 1101, 1103 and 1104 in Table 2. However, if the percentage of resin in the prepreg varies significantly, the determination of the enthalpy without correction fails to give reproducible values and in these cases, the correction for the mass of resin gives better

results (batches 1014 and 1010).

A decrease of enthalpy indicates an advancement of the curing reaction. On this basis, the different batches may be arranged in the following order: 1047 > 1023 > 1101 ~ 1014 ~ 1104 ~ 1010 > 1103. The enthalpy for the two samples of neat epoxy resin (batches 1047 and 1023) is somewhat larger than for the prepreg. There are two possible explanations for this. Firstly, the impregnation process usually involves heating, thereby causing some advancement of the epoxy resin. Secondly, it has been reported [18] that the presence of reinforcing fibres (in that particular case, glass) in the resin affects the cure kinetics and gives a lower enthalpy of cure.

In reverse-phase liquid chromatography [10], using the peak corresponding to the reaction product involving one molecule of TGDDM and one molecule of DDS, the order for the different batches was the following: 1047 < 1104 < 1103 ~ 1014 < 1101 ~ 1010 < 1023. This arrangement is somewhat different from that found with DSC. In comparison, the order found by infrared spectroscopy (attenuated total reflection) using an index based on the area of epoxy peaks is 1047 > 1101 > 1014 ~ 1010 > 1104 > 1103, which corresponds fairly well to the DSC order.

In both DSC and IR, the final result is a global measurement over all molecules containing epoxy groups, whereas in RPLC the order of advancement is determined from a specific compound without taking into consideration the influence of other compounds. The good agreement between DSC and IR suggests that infrared spectroscopy could possibly be used as a faster method to evaluate the degree of advancement.

Aging of the Narmco 5208/WC3000 prepreg

Sheets of Narmco Rigidite 5208/WC3000 prepreg (batch 1014) were suspended in a room maintained at 22°C and 50% relative humidity for 66 days. Selected samples of aged prepreg were analysed by differential scanning calorimetry as described previously. For each sample, two to four specimens were measured. After the DSC measurement, the exact weight of resin in the specimen used was determined by the thermogravimetric method developed here. The results are summarized in Table 3.

It is seen that the percentage of resin varies significantly from specimen to specimen. The values range from 38.6% to 46.6%, even though all specimens came from the same batch of prepreg. The variation of enthalpy as a function of exposure time is plotted in Figure 11. Using the "uncorrected" values, it can be seen that there is a gradual decrease with aging time, but there is a large degree of scatter which would make it very difficult to accurately estimate the extent of aging by this method. When the corrected values are plotted, the degree of scatter is much reduced. Linear regression gives a correlation coefficient of 0.95, as compared to 0.63 for the "uncorrected" case. The equation obtained is:

$$\Delta H\ (J/g) = 560.6 - 1.449 \times (\text{number of days exposure})$$

This shows that ΔH, which is directly related to the number of unreacted epoxy groups in the resin, decreases by 0.26% per day from its initial value of 561 J/g. This is somewhat lower than the figure of 0.34% obtained by infrared spectroscopy [10], which in theory is also related to the number of unreacted epoxy groups. One possible reason for the discrepancy is that two different epoxy resins are involved in the Narmco 5208 system,

and the bisphenol A Novolac epoxy appears to react faster than the TGDDM-based one. If the two resins make different relative contributions to the IR epoxy index and the heat of polymerization, this may explain the difference between the results obtained by the two methods.

In spite of the reasonably good correlation obtained, DSC appears to be less sensitive than IR or RPLC for detecting small changes in composition, such as those which occur in the first 20 days of aging. It also requires considerably more time, because of the thermogravimetric analysis needed to obtain reproducible ΔH values.

CONCLUSIONS

A dynamic thermogravimetric method has been developed with oxygen as atmosphere in order to accurately determine the percentage of resin in a carbon-epoxy prepreg. The inflexion point corresponding to the end of oxidation of the epoxy resin and to the beginning of oxidation of the carbon fibres is used to directly evaluate the mass of resin in the sample used. This quantity is then used in combination with differential scanning calorimetry results to calculate the enthalpy of the curing reaction in an epoxy resin. Reproducible values of enthalpy can be obtained if the DSC thermogram is measured under a nitrogen atmosphere and the mass of resin is determined by means of thermogravimetric analysis. This method is an excellent application for a combined TGA-DSC instrument since the many manipulations leading to weight errors can be reduced and substantial savings in time can be achieved.

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Table 1: Thermogravimetric results obtained with known mixtures of epoxy resin and carbon fibres.

Mixture preparation data			TGA experimental results		
Mass carbon (mg)	Mass resin (mg)	% resin	% resin (point 1)	% resin (point 2)	% resin (point 3)
22.5	15.2	40.3	36.8	36.5	40.2
19.2	30.9	61.7	57.8	56.6	61.6
13.7	6.4	31.8	27.7	29.7	32.0
37.3	28.4	43.2	39.7	38.6	43.3

Table 2: Thermal analysis results for different batches of Narmco 5208/WC3000 prepreg.

#	Batch	Weight loss DSC %	% Resin	ΔH uncorrected (J/g)	ΔH corrected (J/g)
1	1014	2.2	44.6	581	548
2	1014	1.2	40.0	526	552
3	1014	2.7	42.8	555	545
4	1103	3.2	40.4	517	536
5	1103	2.9	42.0	517	517
6	1010	2.8	47.0	614	548
7	1010	4.3	42.5	548	542
8	1101	3.7	43.6	567	546
9	1101	4.3	44.5	588	555
10	1104	4.2	40.5	524	544
11	1104	3.5	40.1	526	551
12	1023	---	100.0	---	568
13	1023	---	100.0	---	563
14	1047	---	100.0	---	620
15	1047	---	100.0	---	612

Table 3: Thermal analysis results for aged prepreg samples.

Prepreg aging time (days)	DSC wt. loss (%)	% Resin by wt.	ΔH (uncorrected) (J/g)	ΔH (corrected) (J/g)
0	2.2	44.6	581	548
0	1.2	40.0	525	552
0	2.7	42.8	555	545
7	4.1	41.5	540	546
7	4.1	43.6	577	556
17	3.6	40.3	507	529
17	0.0	39.3	526	562
17	3.1	39.2	515	552
17	3.6	39.2	513	549
32	4.4	45.0	554	516
32	2.7	38.6	478	520
42	3.0	45.1	530	494
42	2.6	42.4	506	501
59	4.5	46.6	512	462
59	4.4	46.1	511	465
66	3.6	43.9	494	472
66	0.4	45.5	498	460
66	3.8	45.0	504	470

LIST OF FIGURES

Figure 1: TG curve of Narmco 5208 neat epoxy resin. Gas: nitrogen; heating rate: 10°C/min; mass of resin: 22.4 mg.

Figure 2: (A) TG curve (with derivative) of Narmco 5208 neat epoxy resin; (B) enlarged area. Gas: oxygen; heating rate: 10°C/min; mass of resin: 32.6 mg.

Figure 3: TG curve of carbon fibres. Gas: oxygen; heating rate: 10°C/min; mass of fibres: 24.1 mg.

Figure 4: TG curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 54.9 mg.

Figure 5: (A) Isothermal TG curve of Narmco 5208 prepreg. Gas: oxygen; temperature: 500°C; mass of prepreg: 47.7 mg. (B) Isothermal TG curve of a prepared mixture of epoxy resin (65.2% w/w) and carbon fibres (34.8% w/w). Gas: oxygen; temperature: 420°C; mass of sample: 65.3 mg.

Figure 6: (A) TG curve of a prepared mixture of epoxy resin (40.3% w/w) and carbon fibres (59.7% w/w); (B) enlarged area. Gas: oxygen; heating rate: 10°C/min; mass of sample: 37.7 mg.

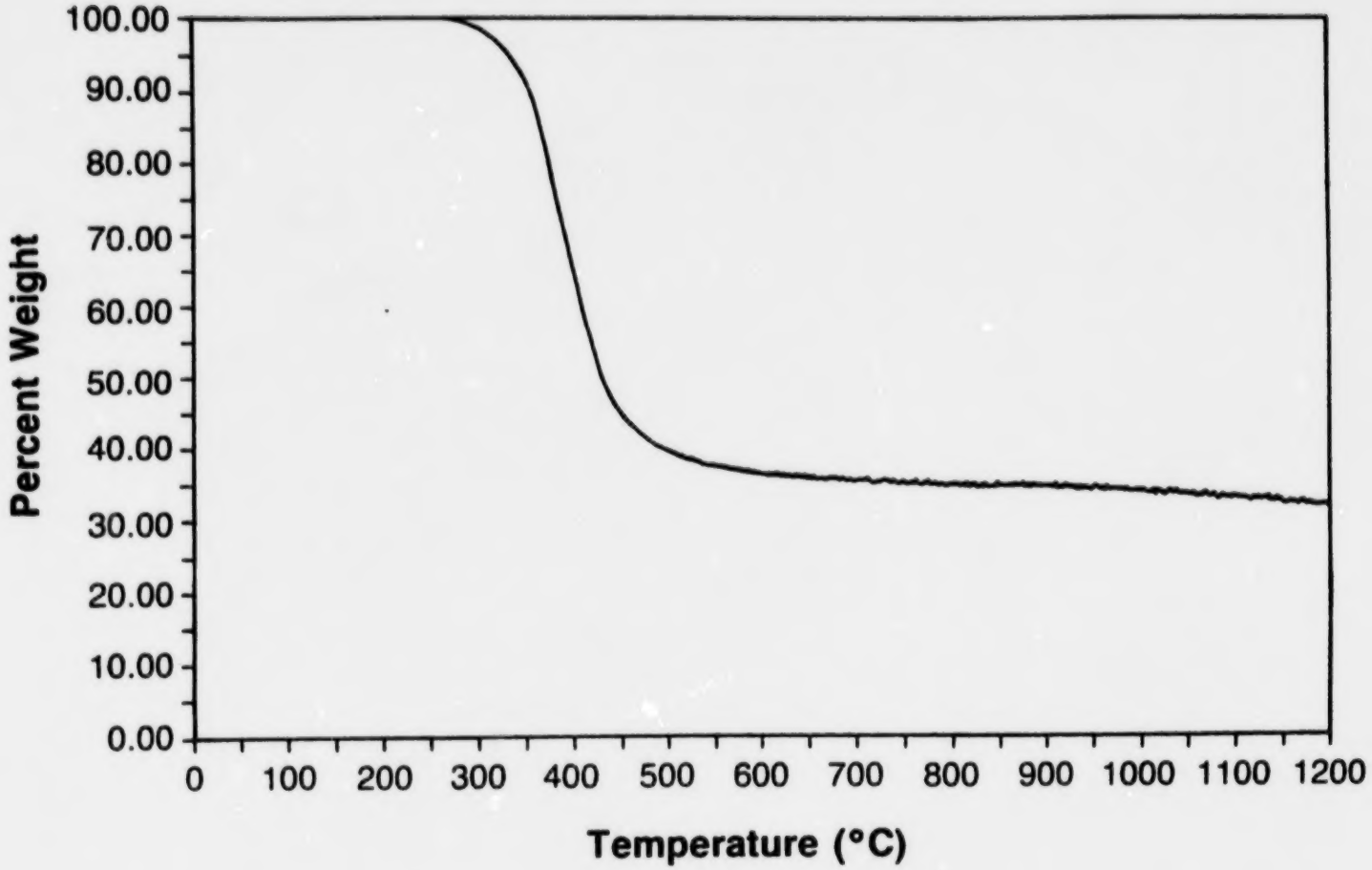
Figure 7: TG curve of Narmco 5208 prepreg. Gas: air; heating rate: 10°C/min; mass of prepreg: 63.5 mg.

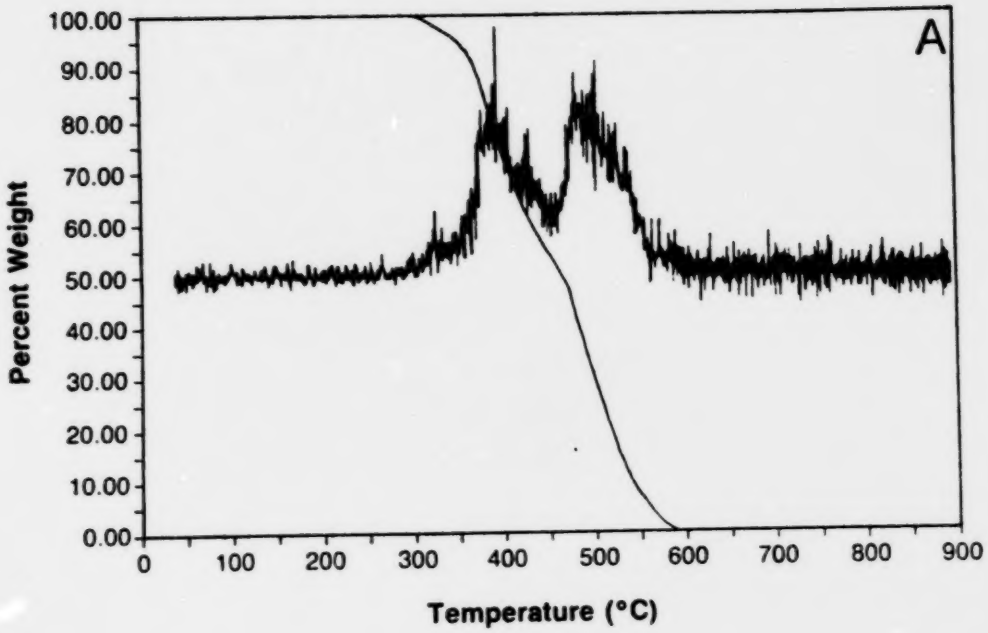
Figure 8; DSC curve of Narmco 5208 prepreg. Gas: static air; heating rate: 5°C/min.

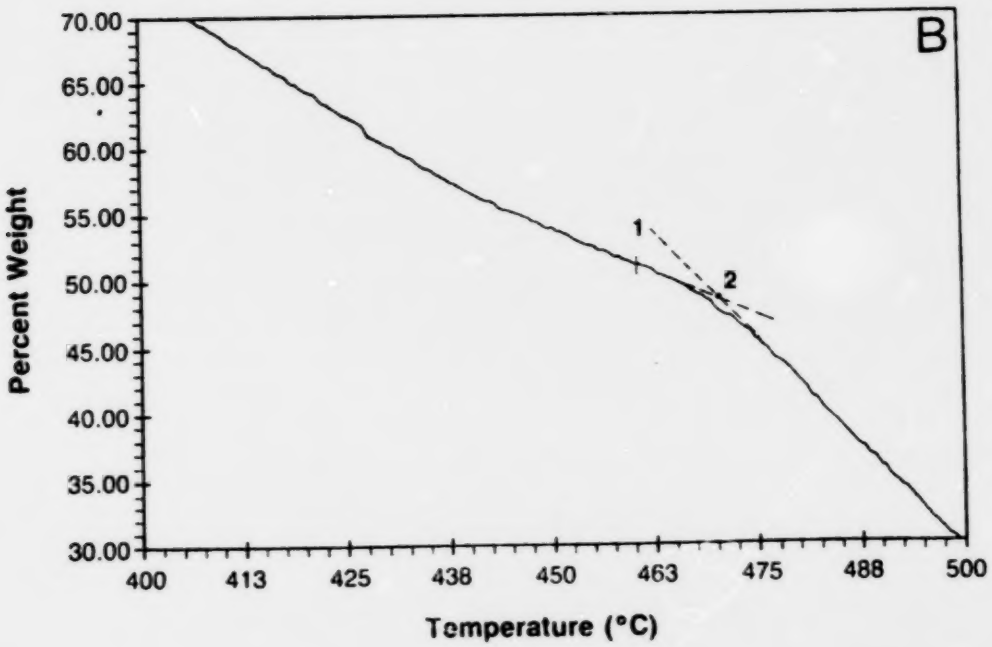
Figure 9: TG curves of Narmco 5208 prepreg. (A) Gas: nitrogen; heating rate: 10°C/min; mass of prepreg: 30.5 mg. (B) Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 37.2 mg.

Figure 10: DSC curve of Narmco 5208 prepreg. Gas: nitrogen; heating rate: 5°C/min.

Figure 11: Variation of ΔH as a function of prepreg exposure time; (◇) uncorrected; (■) corrected.


Percent Weight
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
Temperature (°C)


A
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Weight
0
100
200
300
400
500
600
700
800
900
Temperature (°C)


B
70.00
65.00
60.00
55.00
50.00
45.00
40.00
35.00
30.00
Percent Weight
1
2
400
413
425
438
450
463
475
488
500
Temperature (°C)

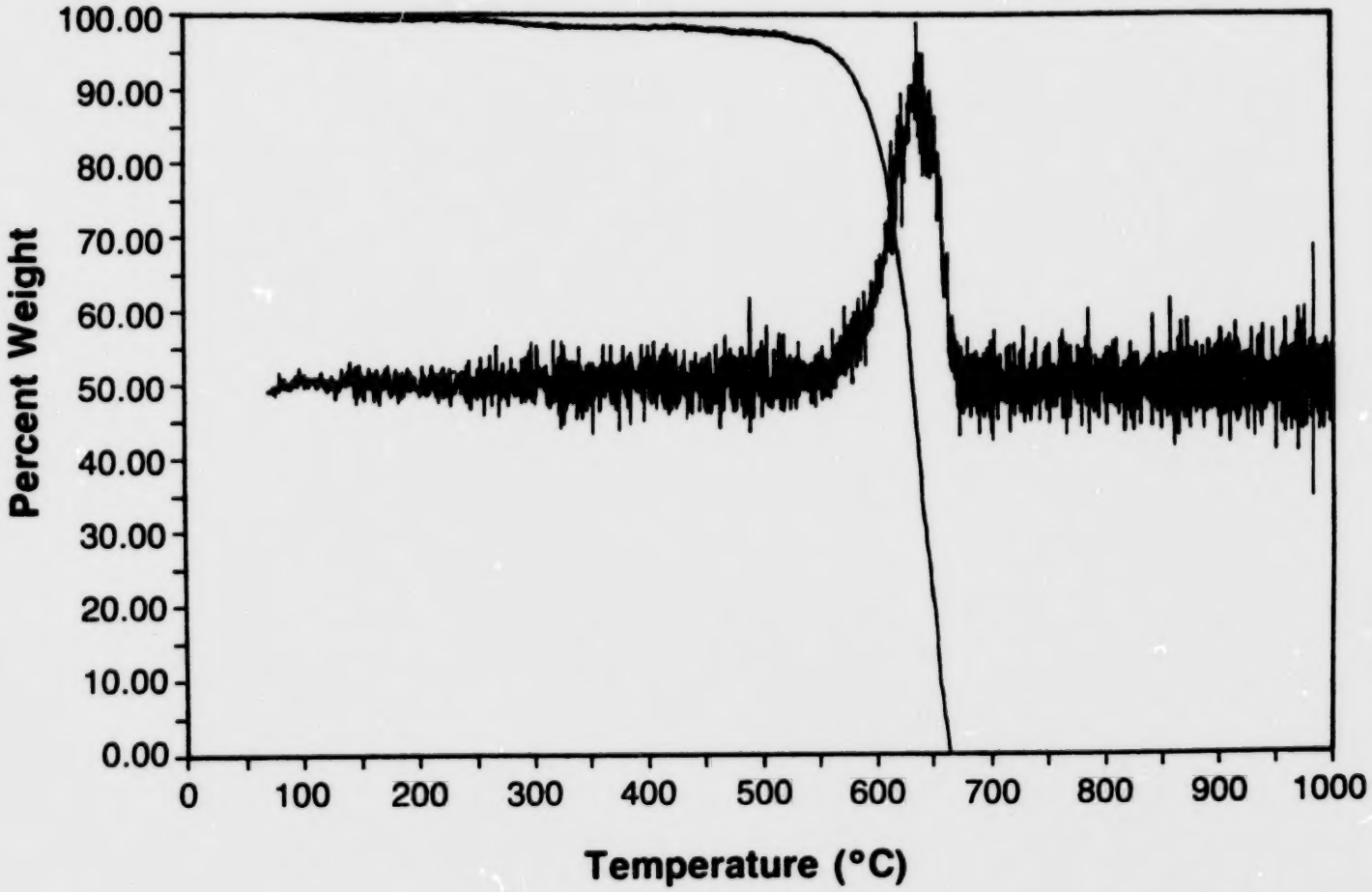
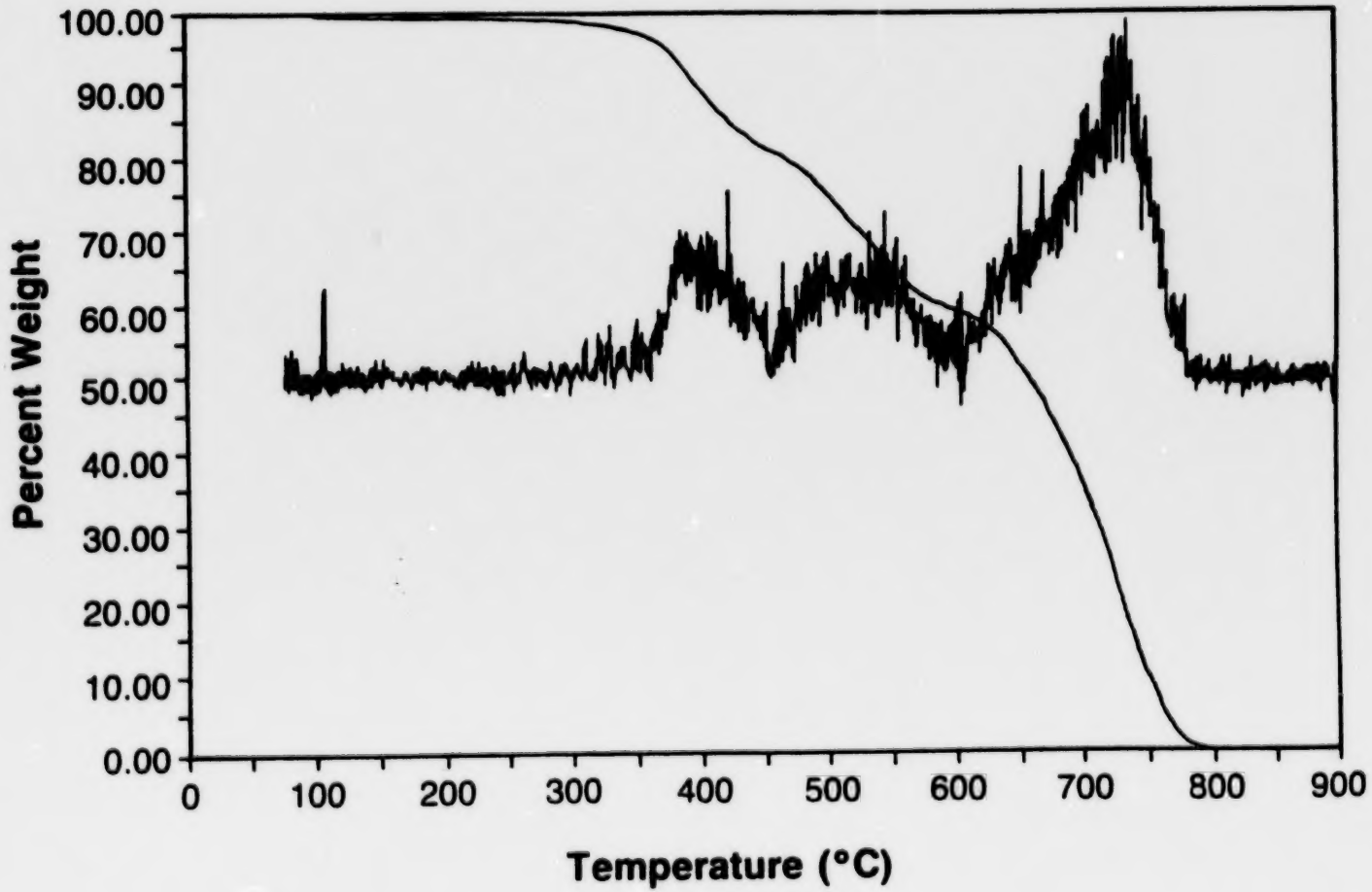
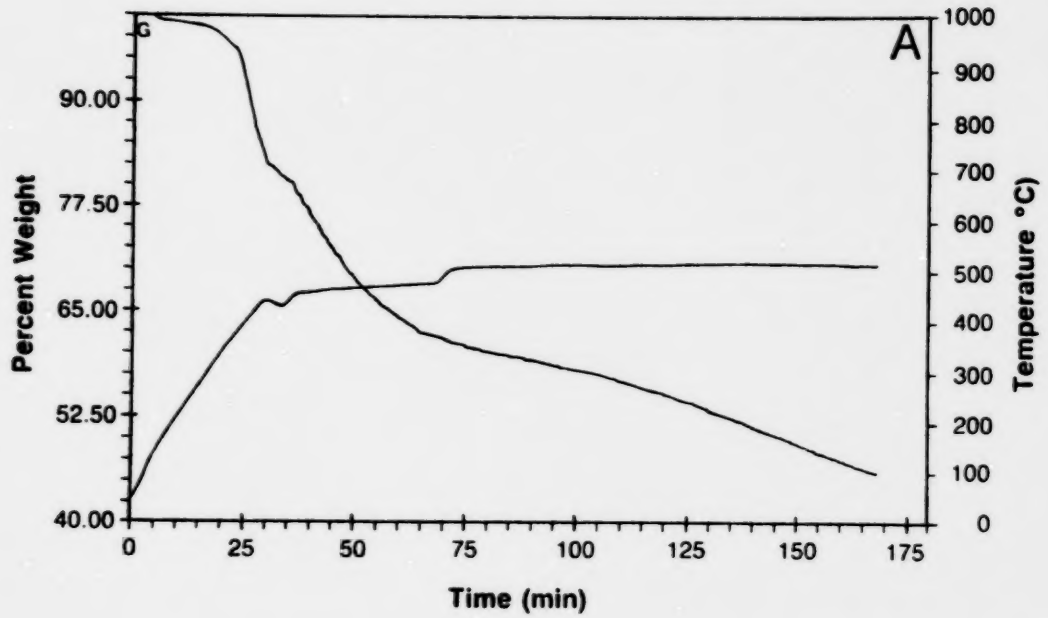

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Weight
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

Fig. 3


100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Weight
0
100
200
300
400
500
600
700
800
900
Temperature (°C)


A
Percent Weight
90.00
77.50
65.00
52.50
40.00
0
25
50
75
100
125
150
175
Time (min)
1000
900
800
700
600
500
400
300
200
100
0
Temperature °C)

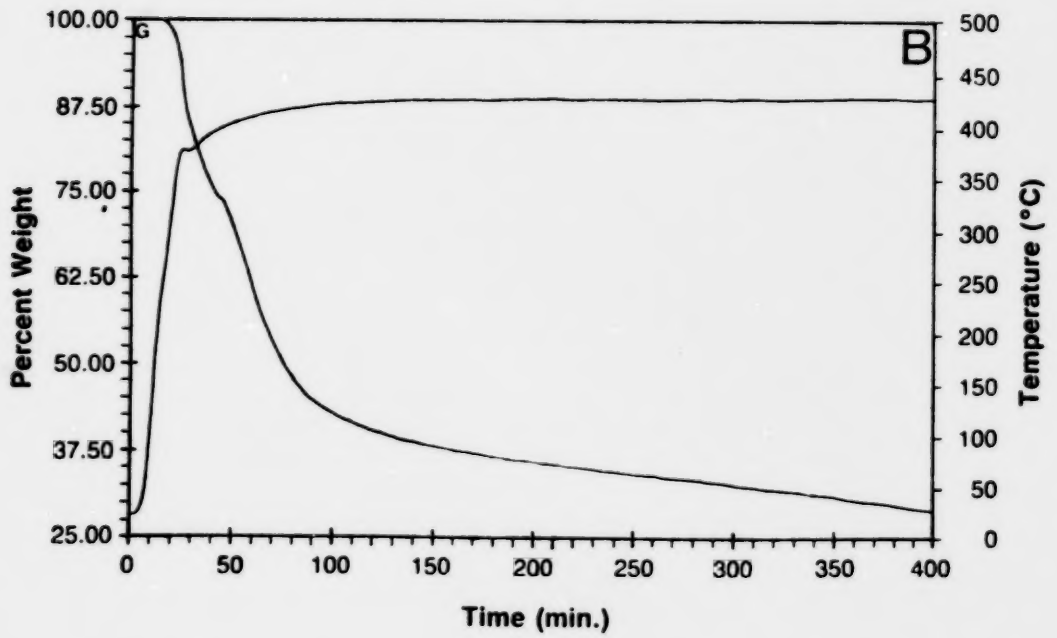
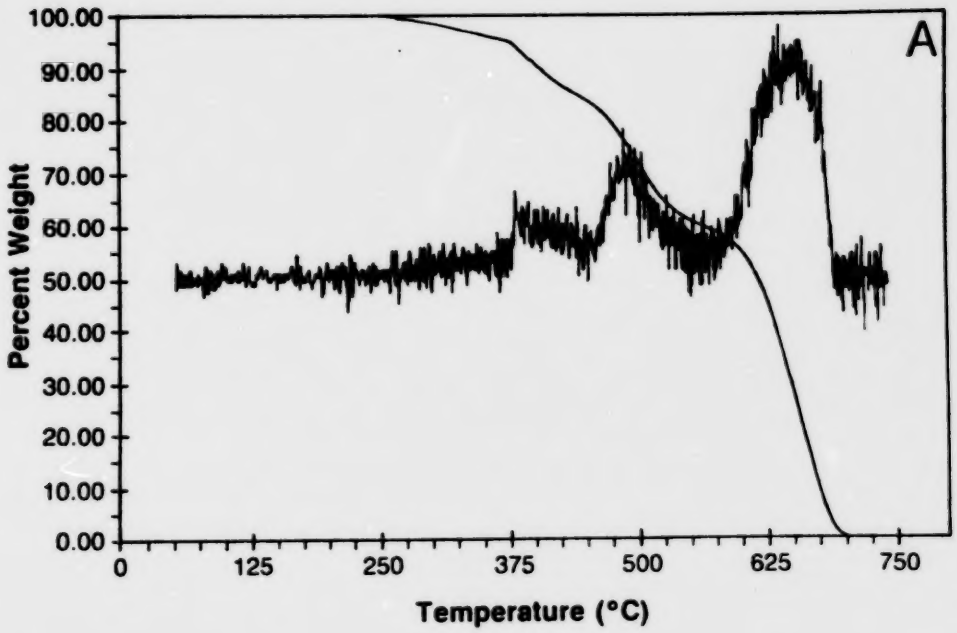

B
Percent Weight
100.00
87.50
75.00
62.50
50.00
37.50
25.00
0
50
100
150
200
250
300
350
400
Time (min.)
500
450
400
350
300
250
200
150
100
50
0
Temperature (°C)

Fig.5


A
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Weight
0
125
250
375
500
625
750
Temperature (°C)

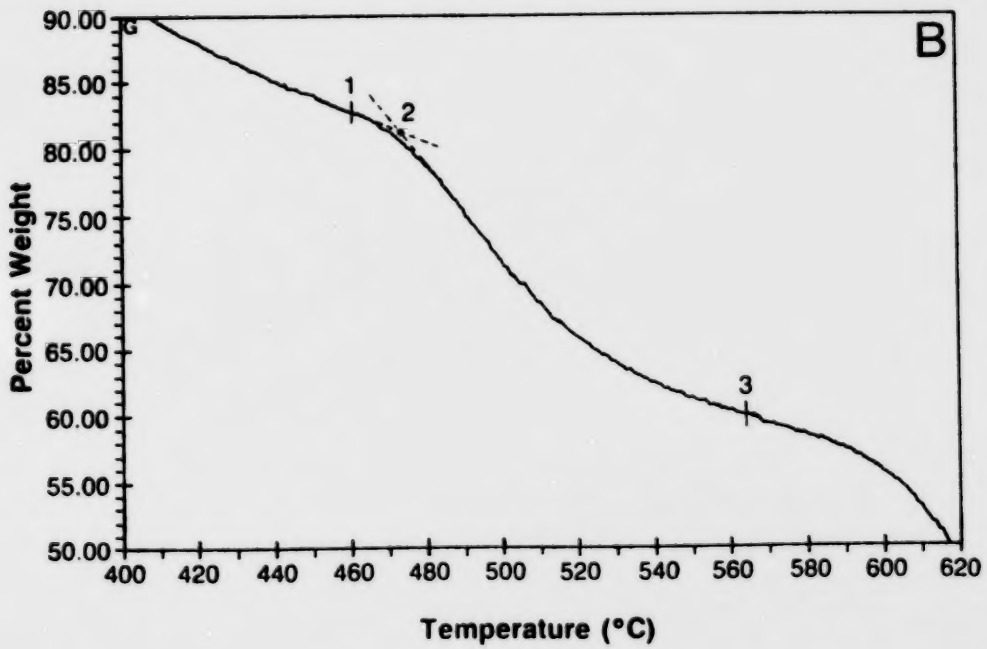

B
90.00
85.00
80.00
75.00
70.00
65.00
60.00
55.00
50.00
Percent Weight
1
2
3
400
420
440
460
480
500
520
540
560
580
600
620
Temperature (°C)

Fig.6

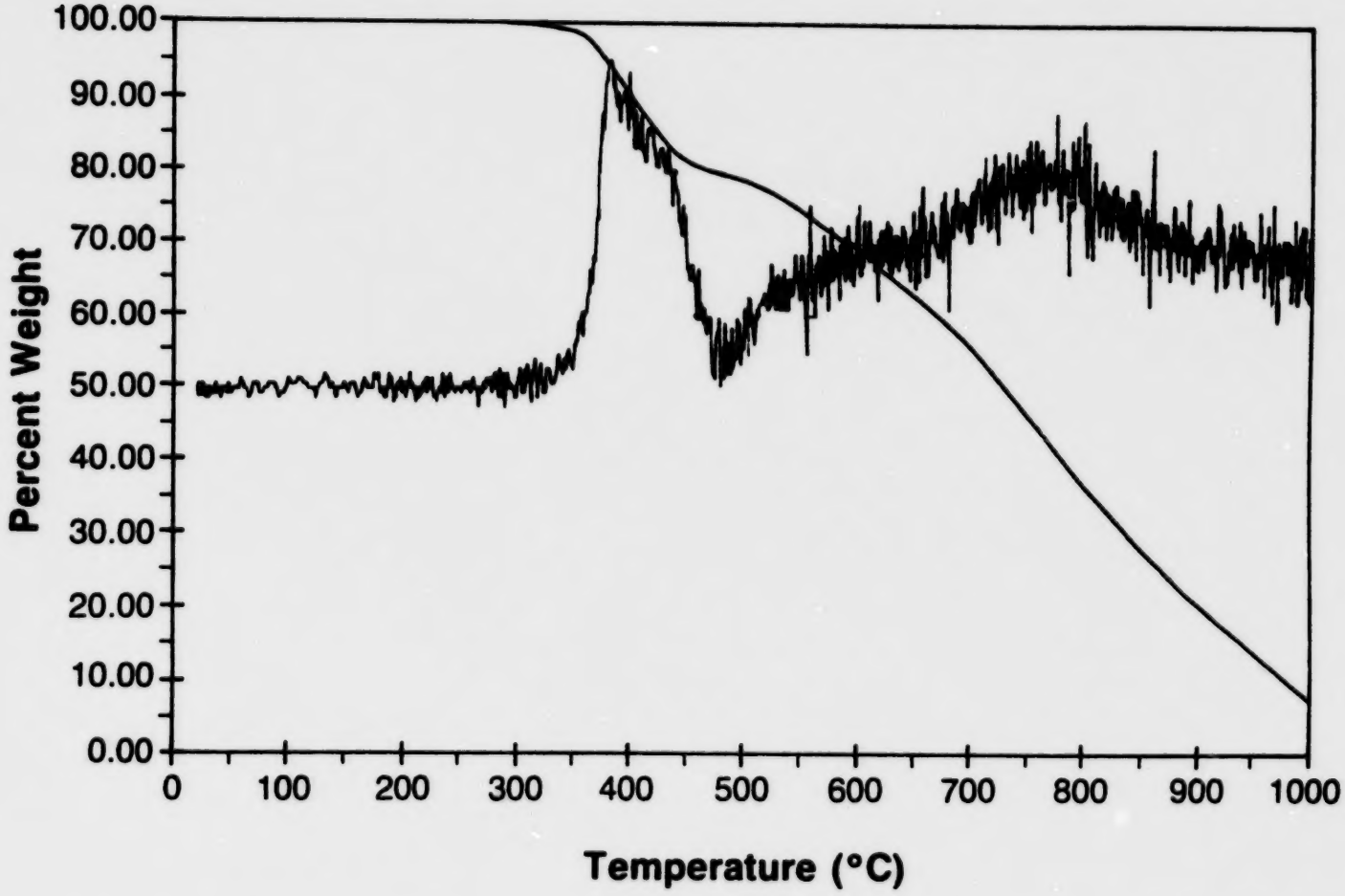
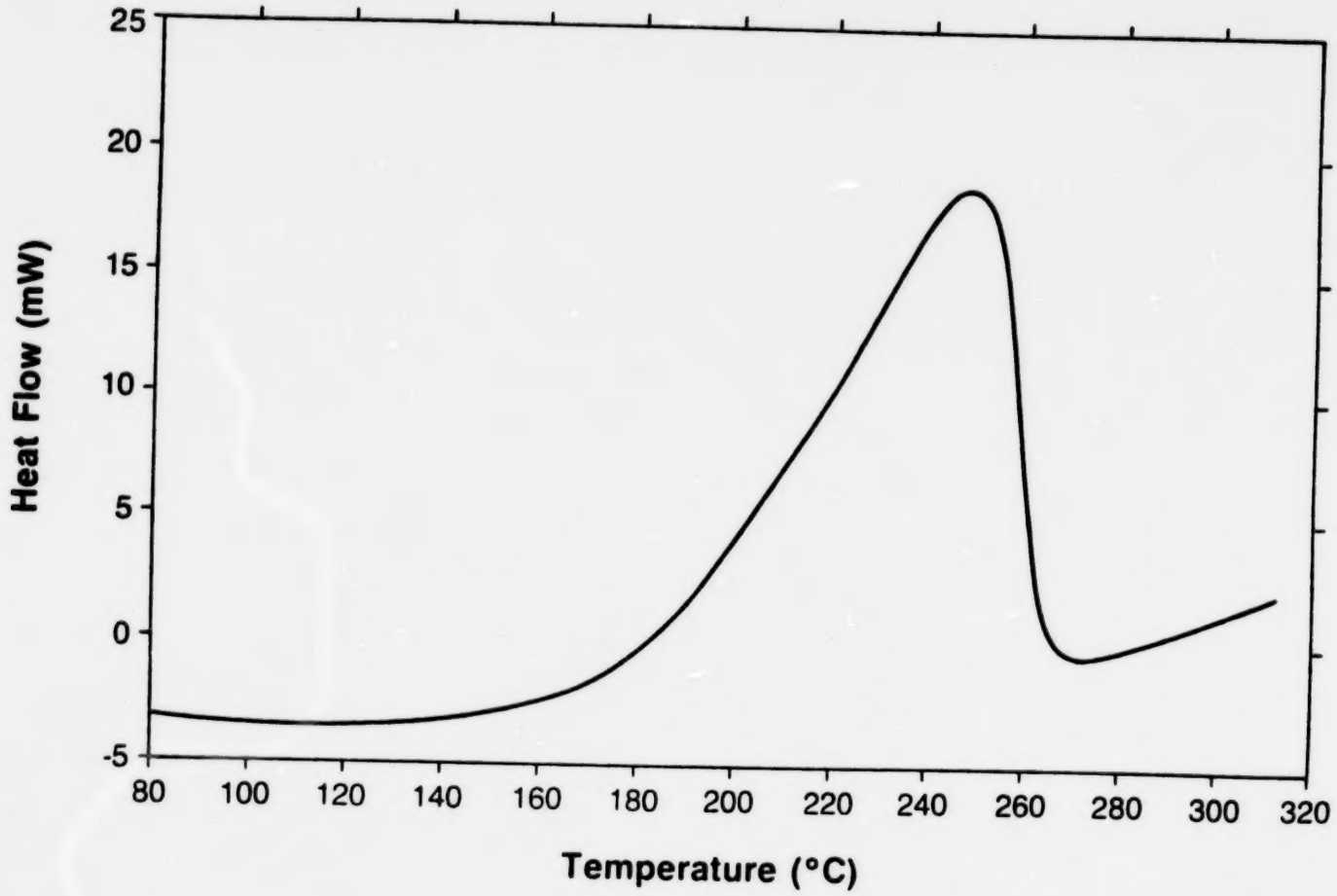

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Percent Weight
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

Fig 7


Heat Flow (mW)
25
20
15
10
5
0
-5
80
100
120
140
160
180
200
220
240
260
280
300
320
Temperature (°C)

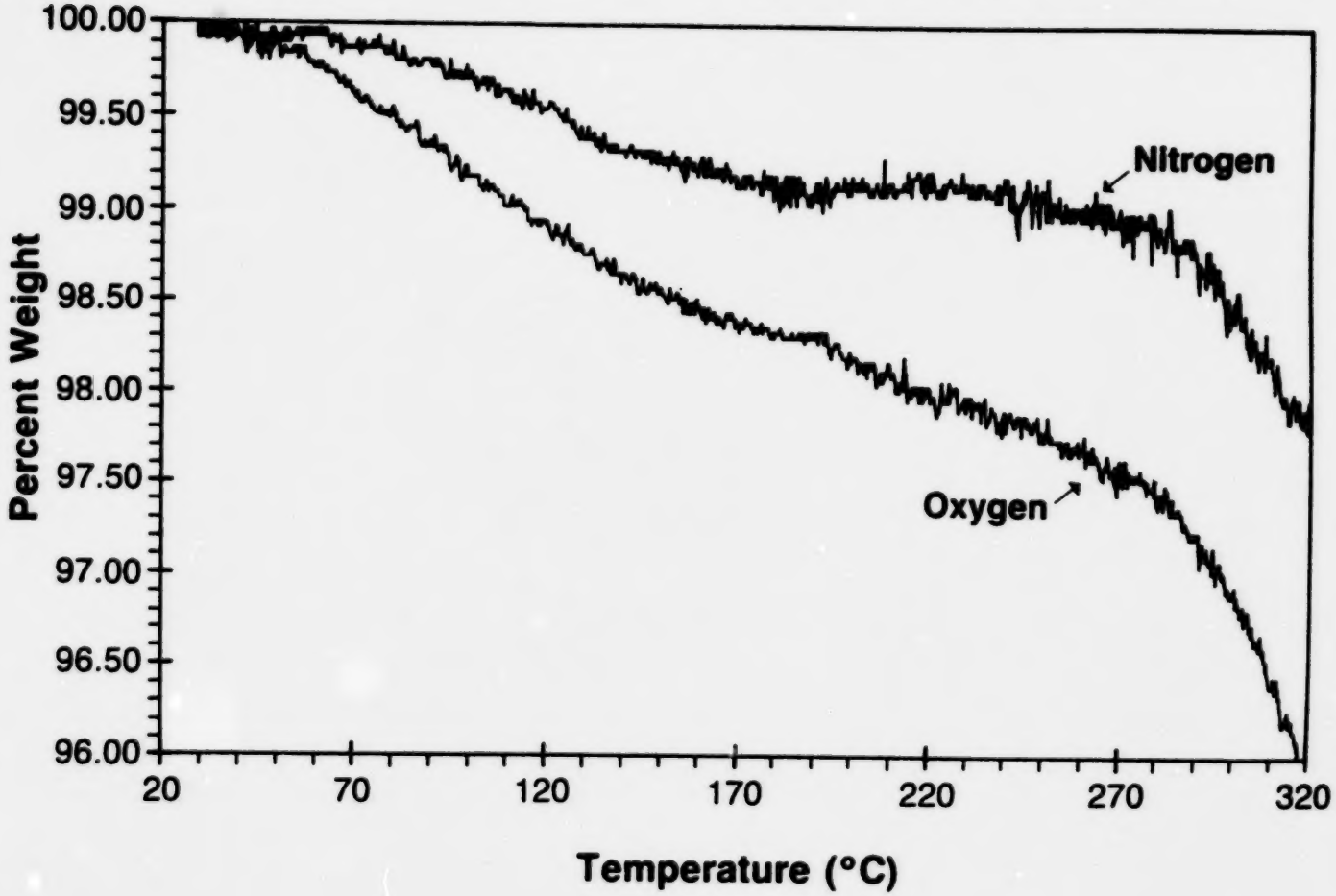
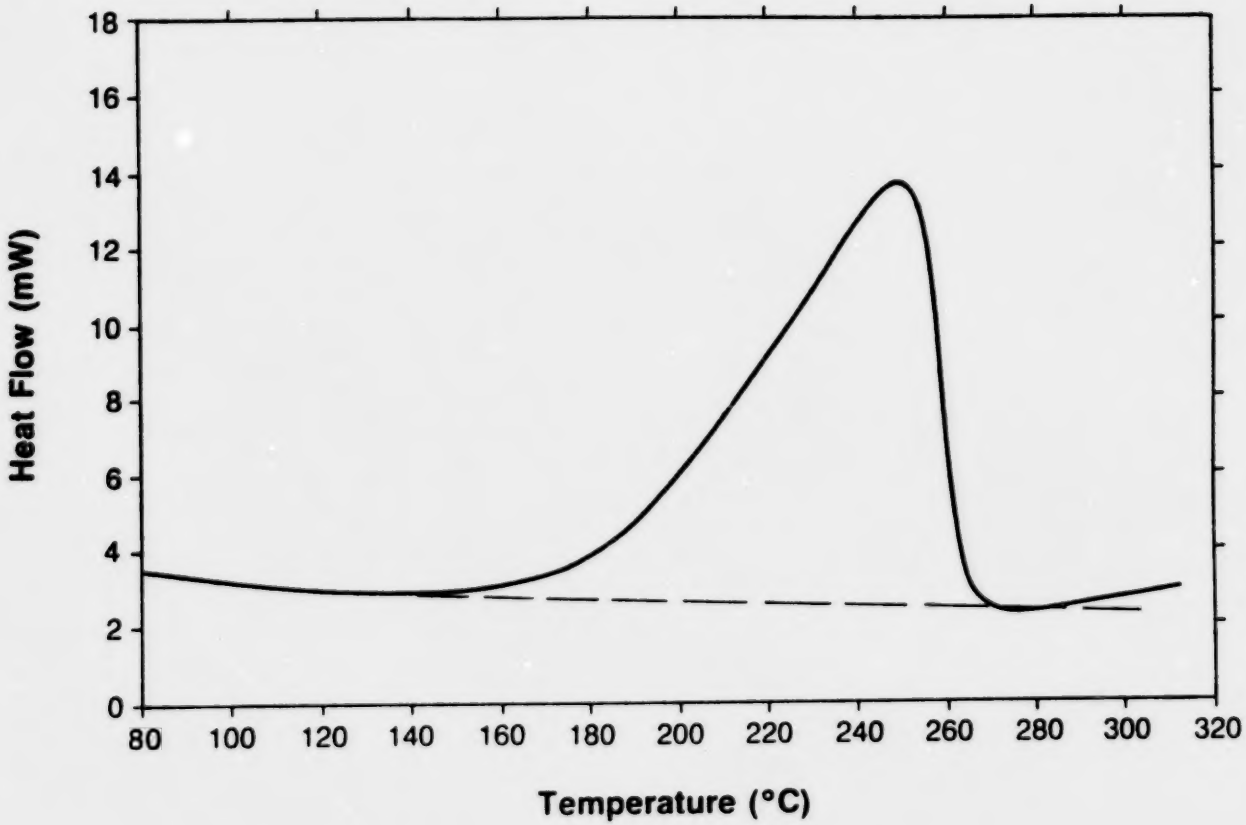

100.00
99.50
99.00
98.50
98.00
97.50
97.00
96.50
96.00
Percent Weight
20
70
120
170
220
270
320
Temperature (°C)
Nitrogen
Oxygen

Fig 9


Heat Flow (mW)
18
16
14
12
10
8
6
4
2
0
80
100
120
140
160
180
200
220
240
260
280
300
320
Temperature (°C)

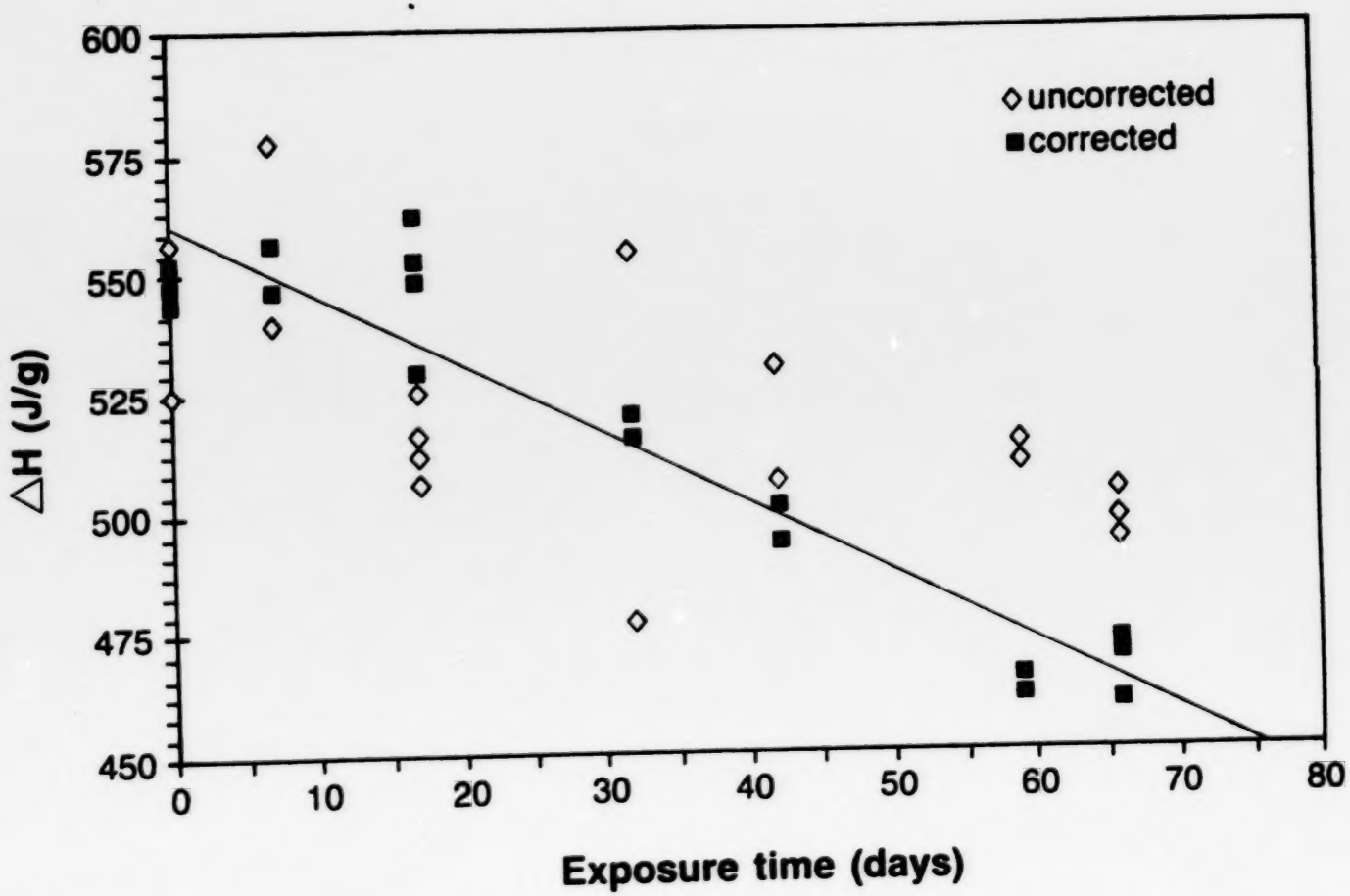

600
575
550
525
500
475
450
△H (J/g)
0
10
20
30
40
50
60
70
80
Exposure time (days)
◇uncorrected
■corrected

Fig. 11